Aalto University
School of Chemical
Technology

School of Chemical Technology
Degree Programme of Forest Products Technology

Nicolás Cadena Moreno

DEVELOPMENT OF DISSOLVED AIR FLOTATION FOR MINING WASTEWATERS PURIFICATION

Master's thesis for the degree of Master of Science in Technology

Submitted for inspection, Espoo 30th of September 2016.

Supervisor **Prof. Olli Dahl**

Instructor **Ph.D. Anup Gurung**

Author Nicolás Cadena Moreno

Title of thesis DEVELOPMENT OF DISSOLVED AIR FLOTATION FOR MINING WASTEWATERS PURIFICATION

Department Department of Forest Products Technology

Professorship Environmental Management **Code of professorship** KM3004

Thesis supervisor Prof. Olli Dahl

Thesis advisor(s) / Thesis examiner(s) Ph.D. Anup Gurung

Date 30.09.2016 **Number of pages** 50 **Language** English

Abstract

Modern mining uses vast amounts of water for the recovery of valuable metals. As the associated costs associated to fresh water price and wastewater treatment continue to increase, there has been a prolonged interest in reusing the mine effluents for the extraction processes. However, wastewater reclamation is challenging as many of the pollutants in the effluents decrease the efficiency of the recovery. Moreover, the huge volume of the effluents greatly reduces the number of suitable purification processes.

The present study tested the feasibility of using dissolved air flotation (DAF) for removing one of the most common pollutants in mining wastewaters: xanthates. The removal capability was evaluated using a general statistical factorial experiment design over two sets of jar tests. The experiments evaluated xanthate reduction with pH, flocculant type, and origin of wastewater (process water and thickener overflows from two different flotation circuits) as independent variables. The best performing conditions were scaled up and further examined using DAF over of settling.

Results demonstrate that it is possible to remove xanthate from the effluents of the thickener overflow using DAF, with average reductions of approximately 50%. It was also observed that the source of wastewater has the largest impact on the process and exhibits an important interaction with the type of flocculant. Overall, DAF has the potential to increase water recirculation in mining operations.

Keywords Mining effluents, mining wastewater, xanthate, potassium ethyl xanthate, KEX, jar tests, dissolved air flotation, microbubbles, flocculation, flocculants

ACKNOWLEDGEMENTS

This study was conducted for Aalto University Department of Forest Products Technology and for Outotec Oyj. Special thanks to Professor Olli Dahl and M.Sc. Kaj Jansson for their continuous support and recommendations for the research.

NOMENCLATURE

A100	Commercial anionic flocculant
ANOVA	Analysis of variance
C471	Commercial low-cationic flocculant
COD	Chemical oxygen demand
CS_2O	Xanthate group
DAF	Dissolved Air Flotation
DS	Dissolved solids
EPA	United States environmental protection agency
FQM	First quantum minerals
HPLC	High performance liquid chromatography
IC	Inorganic carbon
IMO	International maritime organization
KEX	Potassium ethyl xanthogenate
MIBC	Methyl isobutyl carbinol
N200	Commercial non-cationic flocculant
NDM	Northern dynasty mines
p	p-value
PAC	Polyaluminum chloride
TC	Total carbon
TOC	Total organic carbon
TS	Total solids
TSF	Tailings storage facility
TT	Thickened tailings
UV-VIS	Ultraviolet-visible (spectrophotometry)

CONTENTS

1
INTRODUCTION

Modern mining heavily relies on froth flotation for the extraction of minerals such as copper, nickel, lead, silver, and gold. In said process, the valuable minerals are separated from the gangue based on their water-flotation properties. Although high recoveries are achieved, vast volumes of water are required for its operation, and the water demand continues to increase. This results in increased environmental impacts and higher operation costs, both in terms of fresh water cost and disposal of contaminated effluents. As such, reclamation and reuse of the resulting wastewater has become an important topic of research in collection of valuable minerals.

Yet, water recycling in froth flotation is far from simple. It is well known that the water quality has a significant impact on the selectivity and efficiency of the process and mine operators prefer to avoid variations in the water quality (Slatter et al, 2009). In summary, contaminants in the water affect the chemistry in the flotation cells, which are designed to use a specific water quality during its operation. For example, while residual xanthates foment unselective flotation, sulfides prevent flotation of the valuable minerals (Rao & Finch, 1989). Moreover, fine suspended solids tend to accumulate in the process and can negatively affect the recovered metal flows. It is difficult to use the wastewater in the process without significantly affecting the efficiency of the same.

Although much research has focused on the removal of suspended solids, or tailings dewatering, little research is available for the removal of dissolved compounds, such as excess mill reagents. The conventional approach relies on passive treatment by building a dam to contain the wastewater, naturally degrade the pollutants, and settle the suspended solids over long periods of time. The wastewater can, then, be recycled to some parts of the process.

However, there are several drawbacks associated with this method. Firstly, storing such large volumes of water carries great risks. An average of two accidents per year were registered between 2000 and 2009 (Adiansyah, 2015) leading to environmental damages and even inundations in the worst cases. On the other hand, costs associated to the dams are increasing as authorities are stricter and monitoring is required even after activities have long ceased in the mine. These disadvantages will only worsen in the future, with greater demand for minerals and lower grade deposits to mine.

Hence, there has been a prolonged interest in developing alternative methods for treating mining wastewater. The solution should treat the effluents continuously in order to reduce the need to store the wastewater in the dam and should, additionally, be able to remove a wide variety of pollutants, including excess mill reagents.

This thesis tested the feasibility of using dissolved air flotation for removing one of the most common pollutants in mining wastewaters: xanthates. Numerical results show that it is possible to remove about 50% of potassium ethyl xanthate from mill effluents by selecting favorable conditions in the pretreatment (coagulation/flocculation). Additionally, some of the most relevant factors affecting the removal efficiency process of the process were identified and discussed.

The remainder of this work is organized as follows.

Chapter 2 describes the main characteristics of the mining effluents and some of the most widely used techniques employed for their treatment. The pollutants often found in this type of wastewater are also discussed, including excess mill reagents.

Chapter 3 focuses on xanthates and their chemistry. Their fate in water and their environmental impacts are presented, as well as the most relevant strategies for their treatment.

In Chapter 4, dissolved air flotation is introduced in terms of its operation principle and pretreatment requirements. Its applications in municipal wastewater treatment are described, followed by applications in industry with special focus on mining uses.

Chapter 5 summarizes the findings of the literature review and argues in favor of utilizing dissolved air flotation in mining applications for xanthate removal.

In Chapter 6, the experimental part of the study is introduced with the materials and methods. The statistical model employed for analyzing the collected data is also explained.

Chapter 7 presents the results of the study in form of raw data and discussion of the same. The impacts of pH, source of wastewater, coagulant dose, type of flocculant, and their interactions are discussed. The most important findings are presented in Chapter 8 as conclusions.

Finally, Chapter 9 revises the entire thesis for possible improvements in future research and further topics for exploration in the field.

2
FLOTATION EFFLUENTS

Modern mining produces large amounts of waste, especially when low-grade ores are mined. For example, the percentage of mined ore that is discarded as waste is 60% for iron, 99% for copper, and 99.99% for gold (IMO, 2013). This means that a typical industrial gold mine produces more waste in sixteen hours than the entire amount of gold mined through history (Larmer, 2009).

In addition to crushed minerals, the waste contains a massive volume of water. For instance, in copper sulfide refinement about 2.5 to 3 tons of water are required to process 1 ton of mineral containing 0.5% copper (Bleiwas, 2012). The exact amount depends on the specific properties of the ore, including size of the mineral, ore grade, settling rate, amount of clay, and polarity of involved minerals (ibid). In any case, large amounts of water are necessary to recover minerals using froth flotation, which results in vast effluents that require proper disposal.

For the purposes of the following discussion, said effluents are divided in tailings, a mixture of crushed rocks and water, and wastewater, which is the clarified effluent after dewatering operations. Where the term 'effluent' is employed, it should be understood that it refers to tailings and wastewater. Selected features that characterize these discharges are discussed below.

2.1 Selected Characterization Parameters

2.1.1 Temperature

Although temperature has a significant effect on the floatability of ores, most flotation processes are carried at ambient temperatures (Wills & Napier-Munn, 2005) due to economic constrains. Consequently, effluents also have ambient temperatures which can later vary depending on the employed disposal strategy.

2.2.2 pH

The flotation process is commonly conducted at alkaline pH, as collectors (see section 2.2.4) are most stable and corrosion is minimized (Wills & Napier-Munn, 2005). The exact pH depends of the nature of the ore; for sulfide minerals it ranges between 9 and 12 (ibid). This level changes after disposal of the effluents, for example, due to acid mine drainage (AMD) and subsequent neutralization of the resulting flows. Thus, pH varies among the different effluents of the process.

2.2.3 Suspended solids

In froth flotation, solid particles can be divided based on recovery as fine, intermediate, and coarse, with intermediate being that fraction where the best recovery is attained (Ahvininen, 2000). As coarse and intermediate particles are mostly separated before or during the flotation, the tailings suspended solids range between 1 to 600μm (IMO, 2013), and can be classified as sand (larger than 63μm), silt (between 63 and 2μm), or clay (less than 2μm). The latter two fractions are sometimes referred as fines, but concrete ratios depend of the ore properties and extraction process. The suspended solids in the tailings

comprises about 10-20% of the valuable minerals that were not recovered in the flotation and gangue as the balance (NDM, 2005).

In the wastewater, the exact amount of solids depends of the employed tailings management strategies. For example, if conventional tailings (see section 2.2) is used, the effluent comprises about 20 to 40% solids. On the other hand, after using filters the filtrates are virtually free of suspended solids.

2.2.4. Dissolved Pollutants

Several soluble compounds can be found in the flotation effluents. The most common metals include aluminum, arsenic, cadmium, chrome, copper, iron, lead, manganese, mercury, nickel, selenium, silver, and zinc (EPA, 2003). Clearly, the amount of these compounds varies depending on the ore and process characteristics. Furthermore, the effluents often contain cations of ammonia, calcium, magnesium, potassium, and sodium; common anions include nitrate, sulfate, chloride, and carbonate (ibid).

More complex compounds can be introduced during the separation process. Table 1 presents the main flotation reagents, which excesses become pollutants in the effluents. It has been observed that about half of all organic reagents are consumed during the process, whilst the remaining portion leaves the operation in the tailings (Lam, 1999). Not only these species can be found in the wastewater, but many of them break down or react with other species, thus generating further pollutants.

Table 1. Main reagents employed in flotation. Table adapted from Fuerstenau et al, 2007

Type	Description	Examples
Collectors	Surfactants that increase the hydrophobicity of certain minerals by adsorbing to the same. The affected minerals will be more inclined to attach to the bubbles and rise as froth.	Xanthate, dithiophosphate, thionocarbamate, xanthogen formate, xanthic ester
Frothers	Surfactants that stabilize bubbles and reduce surface tension, thus ensuring formation of a stable froth.	Methyl isobutyl carbinol, MIBC, polypropylene glycol, triethoxybuthane, pine oil
Activators	Reagents that modify the surface of a particular mineral in order to improve its interaction with the collector.	Copper sulfate, sodium sulfate, sodium hydrosulfide
Depressants	Prevents collector and/or bubble attachment of certain minerals.	Sodium sulfite, sodium sulfide, sodium cyanide, zinc sulfate, sodium dichromate
pH Modifiers	Modifies the pH of the flotation medium as for controlling selectivity of the separation.	Quick lime, slaked lime, sodium carbonate, sulfuric acid.

2.2.5 Biological Characteristics

Despite fluctuating pH levels, presence of toxic metals, scarce nutrients and sources of carbon, microorganisms can still be found in the flotation effluents. In fact, bacteria, archaea, algae, fungi, yeasts, and protozoa have been observed in different mining mills (Ledin & Pedersen, 1996). Compared with other wastewaters, there is an important presence of iron and sulfur-oxidizing and reducing species due to the medium characteristics. Representative microorganisms include *T. ferrooxidans*, *T. thiooxidans*, *Thiobacillus spp*., *Sulfolobus*, and *Acidianus* (ibid).

Microorganisms in the effluents have a major impact in the mill operations. Firstly, they catalyze reactions that are otherwise very slow. The most widely studied case is AMD, where *Thiobacillus* (Wills & Napier-Munn, 2005) allows oxidation of –mainly- pyrite to sulfate and ferric iron thereby producing acid effluents that are environmentally harmful (Ledin & Pedersen, 1996). On the other hand, it has been reported that *Thiobacillus* and nitrifying bacteria cause serious pitting corrosion problems in the mill (Metropolitan Council Environmental Services, 2007). This is a problem that could be worsened by recycling wastewater, a practice that tends to accumulate bacteria in the system as has been observed in other industries.

2.2 Treatment Methods

Several strategies have been used for disposing flotation effluents, which aim to minimize the risks associated with the waste and reclaim water. The most widely applied techniques are presented below, as tailings and wastewater treatments.

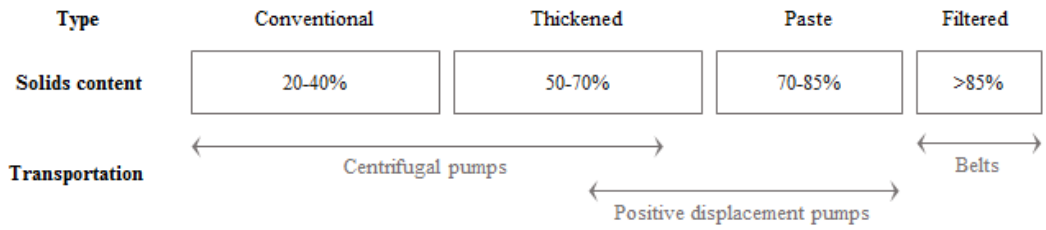


Fig. 1. Indirect tailings disposal methods

2.2.1 Tailings Treatments

Riverine Tailings Disposal

As its name indicates, this strategy consists of releasing the waste directly in a river. This approach was commonly used in the past but as of 2013 there were only four industrial riverine tailings discharges worldwide (IMO, 2013). This reduced amount of existing discharge points is explained by its widely known detrimental environmental impacts, including decline in the diversity and availability of flora and fauna in and around the river, and exposure of metals to humans (ibid).

Submarine Tailings Disposal

Similarly, the submarine tailings disposal strategy discards waste directly in the environment by pumping the tailings to the deep-sea, below the euphotic zone. Unlike the well-known environmental impacts associated with riverine disposal, the consequences of submarine discharges are not fully

understood. It is generally accepted, however, that discharging the tailings destroys the habitat of benthic organisms and disrupts the ecology in that area. Moreover, there are concerns that fine solids would not settle but rather disperse over larger areas (IMO, 2013).

Conventional Tailings

Conventional or tailings dams is the most employed strategy for managing tailings at industrial mines (Adiansyah et al, 2015). The tailings slurry is stored in a valley or impoundment (the tailings storage facility or TSF) for periods of several decades during which sand and silt-sized solids settle, thus separating from the water and forming a layer that resists water movement (NDM, 2005). As such, the potential environmental impacts of tailings are, theoretically, controlled and water can be reused in the mine operations, reducing to a large extent the amount taken from natural sources (Zhang & Stana, cited in Wang et al, 2014). Additionally, the tailings dam is relatively inexpensive and its capital costs can be deferred during operation of the mine, for example, by enlarging the dam wall as more waste is produced.

However, conventional tailings management is not acceptable in many countries because of the risks associated with this practice (Zhang & Stana, cited in Wang et al, 2014). The greatest danger is failure of the dam wall which would release massive amounts of contaminated water, causing floods and polluting nearby water bodies and ecosystems. In fact, authorities are stricter with mine operators banning or requiring further supervision of tailings dams, as two tailings related accidents were registered annually between 2000 and 2009 (Adiansyah, 2015).

Moreover, managing tailings dams has become more and more challenging for mine operators. The increased amount of fine solids in the waste demands longer settling periods and, consequently, larger ponds (Wang et al., 2014). Also, fine gangue particles can retain significant amounts of water which cannot be reused in the process (ibid). Furthermore water evaporation can account to up to 40% of the total water lost on-site, leading some operators to make significant investments for reducing this phenomena (International Council on Mining & Metals, 2012). As tailings dams also require monitoring after closure, some studies have shown that a tailing dam is more expensive than more elaborate processes, such as thickened tailings (Adiansyah et al., 2015).

Thickened Tailings

Thickened tailings (TT) is another approach for managing tailings, where the slurry is dewatered using a thickener before deposition. The resulting solid content in the slurry varies between 50 to 70% depending on the material properties, where fine particles produce moister slurries (Azam, 2004).

Whilst the water recovered as overflow can eventually be reused in the flotation process, the underflow slurry is considered a waste and must be disposed of accordingly. Nevertheless, thickened tailings greatly reduce the TSF size thus requiring smaller dams or, in some cases none at all (Azam, 2004). Furthermore, the risks associated with the TSF are reduced, not only because of the diminished waste volume, but also because TT flow less than conventional slurries.

Despite its advantages, it is not always possible to use a TT strategy for managing the tailings. Particularly, the particle size that is required for the separation at the flotation stage may not be suitable for thickening (Palkovits, 2008), with studies suggesting a limit of 15% fine (less than 20 μm) dry solids content (Verburg, cited in European Commission, 2008). Moreover, presence of some gangue minerals, such as mica, prohibit thickening processes (Palkovits, 2008). An additional factor that discourages use of thickening technologies is its elevated operating cost, which is around 25% higher than conventional slurry disposal (European Commission, 2008).

Paste Tailings

Water content of the tailings slurry can be further reduced using thickeners by producing a paste, a non-segregating state (even after depositing) comprising 70-85% solids that shows little water bleeding at the TSF (Outotec Oyj, 2012). Although filters have been used to produce pastes, modern thickeners are able to produce such underflow using geometries specifically suited for the treated tailings, selected flocculants, and control elements that respond to variations in the feed.

By using this technology more water can be recovered as overflow, thereby reducing by half the space required at the TSF (Outotec Oyj, 2012). Additionally, at the TSF losses of water due to evaporation and seepage are greatly reduced, whilst risks associated with failure of the impoundment are almost eliminated. However, producing a paste is more expensive than TT because of the increasingly complex thickener and the elevated associated operation costs (e.g. pumping). Studies are still debating the long-term costs and benefits compared with the conventional approach (see for example, Adiansyah et al., 2015 and Fourie, 2012), but the capital and operating costs during the lifetime of the mine are often higher than in the conventional tailings case.

Dry Stacking / Filtered Tailings

By using filters is possible to obtain drier tailings, containing more than 85% solids, in a process known as filtered tailings or dry stacking. This method comprises thickening the tailings using an industrial filter to press the water out from the slurry, recirculating the extracted water, and transporting the resulting solid waste to the TSF through belts or trucks. The equipment employed in mineral applications is a belt, disc, or press type filter (Murphy & Caldwell, 2012).

Overall, this technology manages to recover the most water from tailings slurries, whilst producing a cake that can be safely stored by simply dispersing the same in the TSF and, at times, compacting it (Murphy & Caldwell, 2012). However, it is also one of the most expensive options in terms of capital and operating costs (Lupo & Hall, 2010), with the latter being over 40% higher than conventional tailings (European Commission, 2008). These elevated expenses have discouraged use of filtered tailings despite its benefits.

2.2.2 Wastewater Treatment

As seen in figure 2, froth flotation wastewater originates, mainly, from the tailings or concentrate dewatering processes. Although the amount of suspended solids is greatly reduced after said operations, the clarified discharges still require further treatment before its disposal or reuse.

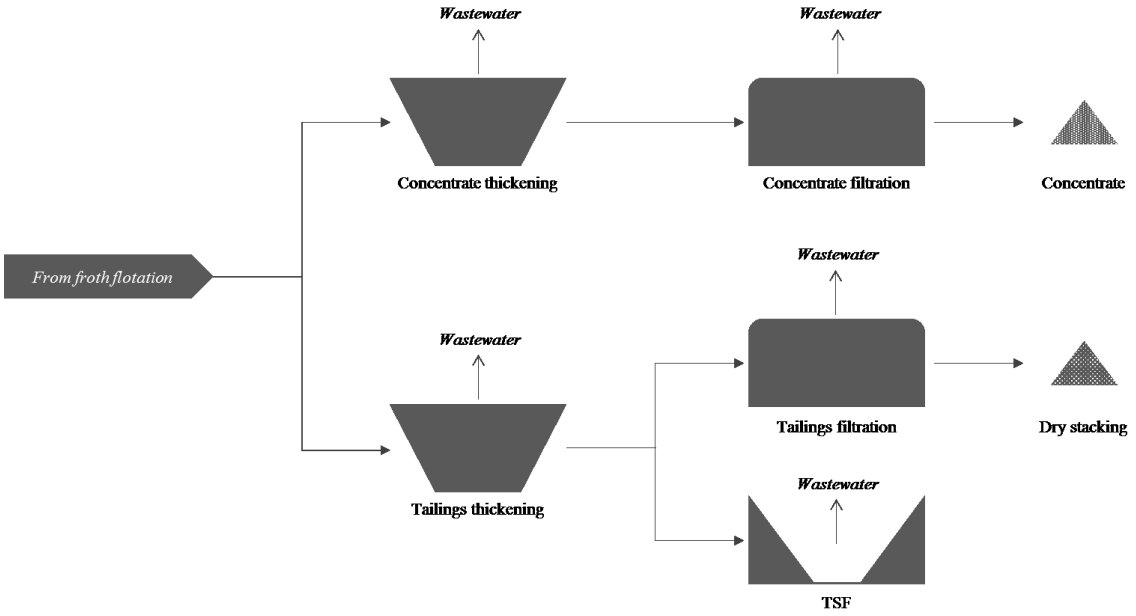


Fig. 2. Schematics of dewatering operations. Figure adapted from Outotec, 2015.

Often addition of lime, limestone or soda is required to neutralize some effluents, particularly for acidic discharges. In addition to raising the pH, some metals precipitate during this addition. However, further treatments are usually required to remove the dissolved metals, including hydroxide precipitation, sulfide precipitation or co-precipitation, which involve adding an appropriate amount of anions and physically removing the resulting solids (EPA, 2003). These processes can occur during the thickening pretreatments -coagulation/flocculation- of the tailings. Other methods to remove metals include ion exchange, reverse osmosis, carbon adsorption, and biological treatments (ibid). The metals concentration targets are usually set according to local legislation.

Sulfates are also removed by precipitation, typically using calcium, barium (Silva et al, 2002) or aluminum salts (Outotec, 2015). Co-precipitation of metals is often observed with this alternative. Membrane filtration is also able to remove sulfate and other anions, although being a more expensive process (Silva et al, 2002). Biological removal is also possible, reducing the sulfate to sulfide and re-oxidizing the same to elemental sulfur (Dries et al, 1998).

Particularly hazardous chemicals should have their own specific treatment. For example cyanide, used in some flotation circuits as iron depressant, is not only highly toxic but exists in several forms in the effluents, including free cyanide, cyanide-sulfur compounds, and metal complexes (EPA, 2003). Depending on the dominant form, the mine operator can include alkaline chlorination, hydrogen peroxide, sulfur dioxide, biological, or natural degradation processes in the wastewater treatment, followed by physical separation (ibid). Another compound that often require a special treatment is arsenic. The main approach is precipitating the same using calcium or iron and removing the precipitate through physical means (Outotec, 2015).

On the other hand, fine solids are commonly removed through filtration, for example through screen, disc, or micro fiber filtration (Outotec, 2015). Dissolved air flotation can also be used to remove fine solids, having removal efficiencies of 90-99% with proper pretreatment (ibid).

Finally, passive treatment is seen as a good alternative for post-closure TSF management and, to a lesser degree, in active mines (EPA, 2003). The technique includes a combination of physical, chemical, and biological processes, such as settling, precipitation, and microbial reduction (ibid). One of those systems can comprise, for example, neutralization followed by deposition in a wetland (ibid). However, these systems often require a significant amount of time to work efficiently, which is not ideal for reclaiming water for the operation of the mill.

.

Purification of flotation effluents is challenging due to the immense amounts of slurry to be treated and the diverse pollutants therein. Moreover these effluents are not homogenous but vary considerably depending on the characteristics of the mined ores, the flotation circuit, and the tailings management strategy. As such, reusing the wastewater in the flotation circuit is problematic as any of said pollutants can affect the chemistry of the flotation circuit, thus reducing the efficiency of the same. It is known, for example, that xanthates and its breakdown products have detrimental effects on flotation of sulfide minerals. These collectors are further discussed in the next section.

3
XANTHATE CHEMISTRY

3.1 General Properties

Xanthates are compounds having the general structure formula shown in Figure 3. Being salts of xanthic acid, their chemistry is closely related to that of dithio acids. Since the first half of the 20th century these compounds have been employed as collectors in the flotation of metal sulfides and, due to their extended use, they have become priority chemicals in many countries (Australian Government Publishing Service, 1995). In flotation circuits, xanthates are most commonly employed as 10% solutions of sodium or potassium salts (ibid) with the alkyl group usually being ethyl, isopropyl, isobutyl, or amyl (Wills & Napier-Munn, 2005).

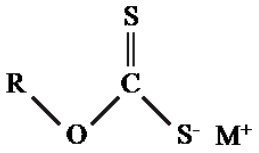


Fig. 3. General structure of a xanthate, where M is K, Na, or H, and R is an alkyl radical.

The main role of xanthate in froth flotation is increasing the hydrophobicity of certain minerals by adsorbing to the same, thus affecting the solid-water interface. Being anionic collectors, the polar group of the xanthate ($S= C–S^-$) reacts with the surface of the mineral, hence leading the hydrocarbon chain (–R) away from the same; the length of this chain increases the efficiency of the process at the cost of decreased selectivity. The mineral that has reacted with the xanthate –now more hydrophobic- can then be separated from the slurry through flotation when it attaches to rising bubbles and forms a froth.

The average froth flotation separation requires about 250 to 350 grams of xanthate per ton of ore (Australian Government Publishing Service, 1995) but not all xanthates react with the minerals. Studies suggest that the waste effluents comprise about 0.2 to 1.2 μg/ml of xanthate (Hawley, cited in Lam, 1999), but values of up to 10 μg/ml have been reported in the literature (Jones, cited in Lam, 1999). This causes two main problems for the mine operators: environmental risks of effluents and water recycle issues.

Firstly, it is widely known that xanthates have negative environmental impacts, particularly being highly toxic to aquatic fauna at low concentrations (Boening, 1998). Moreover, in presence of water, sodium ethyl xanthate (and in general any form of xanthate) can decompose to carbon disulfide, which poses toxic conditions to aquatic environments and has negative effects on human health (Australian Government Publishing Service, 1995). On the other hand, it has been reported that xanthate derivatives inhibit nitrification and are toxic to bacteria employed in wastewater treatment plants (Lam, 1999). As such, effluents containing xanthate cannot be released directly into the environment and could cause problems in conventional wastewater treatment facilities.

Secondly, when water is recirculated residual xanthates and its derivatives have a negative impact on the flotation-separation process. For example, it has been reported that accumulated breakdown products of xanthates result in a greatly reduced selectivity of copper-zinc ores (Ozkan & Acar, 2004). Other derivatives of xanthates also reduce adsorption selectivity on metal sulfides, particularly oxidation products such as dixanthogens (Seke & Pistorius, 2006). Moreover, even non-degraded xanthates can alter the flotation circuit. In lead-zinc flotation the lead sulfide is collected in a first stage whilst depressing the zinc sulfide, which is later collected. The water from the zinc circuit cannot be recirculated to the first flotation because the collectors are different in the two stages and the selectivity of the separation would be compromised (Xingyu et al, 2013). As such, water reuse in flotation has been hindered by the reduced efficiency on the separation caused, partially, by xanthates and its derivatives.

3.2 Detection Methods

There are several options to detect and quantify xanthates in water, including volumetric, gravimetric, potentiometric, and spectrophotometry methods (Lam, 1999). However, the most common and simple alternative is ultra-violet spectrophotometric analysis, where the diothiocarbonate group of the xanthate is detected at 301 nm (Australian Government Publishing Service, 1995). Although the detection limits depend of the equipment, it has been reported that the detection limits range between 0,01mM to 0,2mM for sodium ethyl xanthate (Hao et al, 2008). However, it should be noted that some by-products of xanthate (e.g. dixanthogen and xanthyl thiosulphate) also have absorbance at 301 nm (Ahveninen, 2000) which can affect the estimation of xanthate concentration.

High performance liquid chromatography (HPLC) has been successfully used to measure reaction and breakdown products of xanthate (Lam, 1999; Ahveninen, 2000). Although the different species that arise from xanthate reactions in water can be studied, the residence time in the column of unstable xanthate derivatives could affect the measurement (Ahveninen, 2000). Overall, HPLC is able to yield more specific data about the xanthates in a sample but is more burdensome and less frequently used than the UV spectrophotometric method.

3.3 Chemistry in Water

The fate of xanthates in water greatly depends on the pH of the media, having a greater stability in alkaline conditions (pH 9-11). Conversely, xanthate decomposes in minutes at a pH under 2 (Ahveninen, 2000).

In acidic pH, xanthate reacts with water as follows:

$$ROCS_2M + H_2O \rightarrow ROCS_2H + MOH \quad (1)$$

The xanthic acid formed in the above reaction is unstable and further decomposes to carbon disulphide and an alcohol:

$$ROCS_2H \rightarrow CS_2 + ROH \quad (2)$$

The carbon radical has a major influence on the rate of these reactions, exhibiting slower decompositions with longer alkyl chains (Bulatovic, 2007).

Also favored in acid conditions, xanthate can oxidize to diaxanthogen with several agents (Ahveninen, 2000) as follows:

$$2ROCS_2^- + H_2O + O_2 \rightarrow (ROCS_2)_2 + 2\,OH^- \quad (3)$$

It should be noted that this reaction is not favorable, reaching an equilibrium after 5-10% xanthate oxidation (Australian Government Publishing Service, 1995) and the diaxanthogen readily decomposes to xanthate, carbon disulphide and alcohol as pH increases (Ahveninen, 2000).

On the other hand, neutral and alkaline solutions cause a different path for xanthates dissociation:

$$6ROCS_2^- + 3H_2O \rightarrow 6ROH + CO_3^{2-} + 3CS_2 + 2CS_3^{2-} \quad (4)$$

However, as previously mentioned, xanthates are relatively stable at alkaline conditions and the above reaction is slow. Yet, the alcohol formed during the dissociation catalyzes the same, thereby increasing its rate as reaction advances (Australian Government Publishing Service, 1995).

At very high pH values, xanthates are able to form a variety of compounds (Bulatovic, 2007):

$$ROCS_2K + KOH \rightarrow SC(SK)(OK) + ROH \quad (5)$$

$$ROCS_2K + KSH \rightarrow SC(SK)_2 + ROH \quad (6)$$

$$ROCS_2K + 5KSH \rightarrow 2K_2S + K_2CO_3 + ROH + 2H_2O \quad (7)$$

Another possible chemical reaction of xanthates in process waters is formation of complexes with dissolved metals. These complexes can be soluble or insoluble, with the former being either cationic or anionic (Sihvonen, 2012). The following metals have been observed in stoichiometric complexes with xanthate: Pb^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, and Cu^{2+} (ibid). These metal-xanthate complexes are able to extend the half-life of the collector in water (Boening, 1998).

3.4 Removal Methods

The simplest alternative to eliminate xanthate from water is passive treatment since, as described above, the compound naturally decomposes in presence of moisture and heat (Australian Government Publishing Service, 1995). It should be noted that the breakdown products are still of environmental concern, even riskier than xanthates, but they could then be removed through conventional wastewater treatments. However, this alternative is not always feasible, especially when the wastewater is to be reclaimed since, as previously mentioned, breakdown products also disrupt the flotation process. Furthermore, as the effluents of mining mills are usually alkaline, xanthates are relatively stable and would require many days to fully degrade naturally.

Another possibility is adsorption using liquid-gas interface or activated carbon (Lam, 1999). Although these processes are relatively simple and remove organics efficiently, they are also significantly expensive and require additional maintenance (ibid). Xanthates could also be oxidized with ozone (Xingyu et al, 2013) or ion exchange resins, but once again the process is expensive (Lam, 1999).

Biological treatment of xanthates has been researched, using microbes to oxidize the organics in the effluents (Lam, 1999). Although this alternative is more economical than the physicochemical methods

described above, it is also considerably slower (ibid). As the involved microorganisms require a steady medium to process the organics, this alternative cannot be easily coupled with trending tailings treatment methods (i.e. dry stacking) and would make reclamation of the water more difficult.

One promising method to remove xanthates ions is by adsorption on modified zeolites followed by dissolved air flotation (Oliveira & Rubio, 2008). In a laboratory scale, natural zeolite was activated with sodium and modified with copper as for allowing xanthate adsorption (ibid). After flocculating, the remaining sludge was floated and the xanthates were removed from the effluent. Although the process is highly efficient, it is expected to be expensive due to zeolite production and maintenance costs.

.

Whilst xanthates are essential for collecting sulfide minerals through froth flotation, they can also reduce the efficiency of the process. This occurs when wastewater is reclaimed and recirculated, either in its not-dissociated form, by altering the chemistry in parts of the flotation circuit, or through its derivatives, affecting the selectivity of the flotation. As such, there is a need to remove xanthates from wastewater in a manner that is not only economical but that allows fast reclamation of water within the mill.

4
DISSOLVED AIR FLOTATION

4.1 Background

Dissolved air flotation (DAF) is a clarification process employed for the removal of, mainly, suspended solids, ions, oils, microorganisms, and organics from wastewater, where the separation is achieved using micro-sized bubbles. Usually these microbubbles are formed by dissolving air into water under elevated pressure, and releasing this saturated stream in the flotation tank. Once released, the bubbles attach to the suspended solid particles and rise to the surface, where the resulting sludge can be removed. A schematic representation of a DAF system is shown in Figure 4.

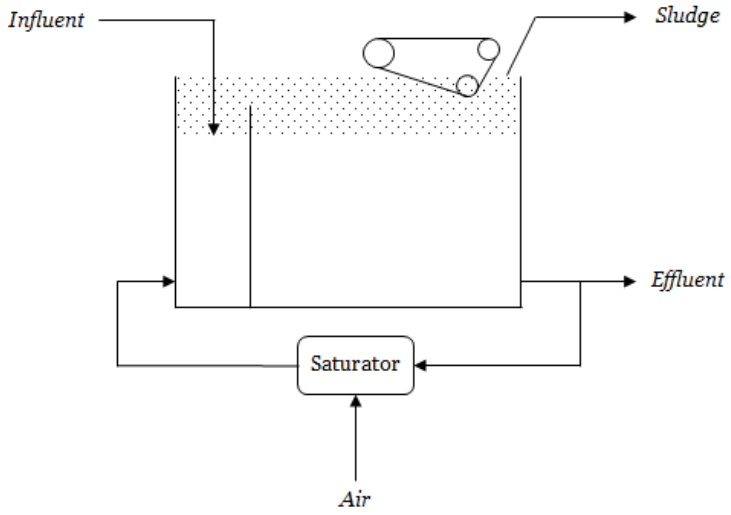


Fig. 4. Simplified schematic representation of a DAF system with recirculation.

The main difference between froth flotation and DAF is the bubble size. Whilst froth flotation usually employs bubbles with a diameter between 600 and 2500 μm, DAF uses bubbles having a diameter between 30 and 100 μm. Consequently the method of producing the bubbles is also different, usually having a fraction of the liquid pressurized with air (or other gas) and suddenly reducing this pressure, thereby releasing said air in form of microbubbles. Operational pressures range between 206 and 620 kPa and the amount of liquid that is pressurized (recycle) ranges between 7 to 30% (Malley, 1988), typically 10% for municipal wastewater treatment (Edzwald, 2010).

Microbubbles provide flotation mechanisms that are unavailable for the coarse bubbles of froth flotation. In addition to the hydrophobic surface forces adhesion, microbubbles are able to nucleate directly at the surface of the particles, regardless of their hydrophobicity (Rodrigues & Rubio, 2007). Furthermore, microbubbles are entrapped inside agglomerations of particles increasing their floatability (ibid). Also, by reducing the bubble size, the contact area between the medium and the bubbles is greatly increased, whilst having a longer residence time in the tank due to their lower buoyancy. This results in an increased probability of contacting the suspended solids.

In most cases pretreatment is necessary for the optimal operation of a DAF plant. Particularly, coagulation and flocculation stages are conducted before entering the flotation tank. As for coagulation, an approximated dose can be estimated based on the TOC of the wastewater, as shown in Table 2. On the other hand, it is recommended to produce flocs smaller than 100μm (Edzwald & Haarhoff, 2012), which are smaller than those required in settling. It should be noted that a realistic dose for both coagulant and flocculants should be determined either through jar tests, based –among other factors- on the removal efficiency of TOC or desired pollutant.

Table 2. Recommended coagulant dose per mg of TOC. [based on Edzwald & Haarhoff, 2012]

Coagulant	**pH 5–6**	**pH 6–7**	**pH 7–7.5**	**pH > 7.5**
Alum (mg Al/mg TOC)	~0.5	0.6 – 0.65	~1	1.3 – 1.8
Ferric (mg Fe/mg TOC)	1.3 – 1.8	2 – 3	3 – 4	N/D
PACl (mg Al/mg TOC)	N/D	0.4 – 0.6	0.7 – 1	> 1

Compared to other clarification techniques DAF has a higher loading rate and a lower requirement of reagents (Crittenden et al, 2012). It also produces a thicker sludge, which is easily dewatered without any intermediate process and its mechanical configuration allows rapid startups (ibid). However, said mechanical configuration is more complex than conventional clarifiers, which results in increased power consumption and more complicated maintenance (ibid). These advantages and disadvantages should be considered when selecting the most appropriate clarification technique, along with the wastewater characteristics.

On this regard, it is generally accepted that DAF is better suited than settling for treating waters having low density particles, low turbidities, and relatively low amount of minerals (Edzwald, 2010). Also, it is more efficient than settling for the removal pathogens and algae (Edzwald & Haarhoff, 2012). These features have resulted in an extensive use of DAF for municipal wastewater treatment.

4.2 Application for Municipal Wastewater and Drinking Water Treatment

DAF is employed in treatment of municipal wastewater and drinking water as an alternative to settling. This process can be implemented as primary or secondary clarification, as well as tertiary treatment (Edzwald & Haarhoff, 2012). For drinking water applications, DAF has been coupled with membrane plants and in desalinization operations (ibid). As of 2008, there were more than 62 large size DAF plants in 18 countries and the amount is increasing (Haarhoff, 2008 cited in Edzwalds, 2010). This interest in flotation as an alternative to conventional sedimentation has resulted in a continuous improvement of DAF plants capacity.

Besides removal of suspended solids, DAF has been successfully employed to treat other pollutants during clarification of municipal wastewater. As tertiary treatment, it has been found to reduce enteric microbial between 90-99%, phosphorus between 55 and 81%, and COD between 28 and 39% (Koivunen & Heinonen-Tanski, 2008). As primary clarification the numbers improve, having 98-99.8% removal for enteric microbes, 90% for total phosphorus, and 47% for COD (ibid).

Another application in municipal wastewater plants, is thickening of excess sludge. The sludge can be thickened from a solids content of 0.5-1% to 3-6%, and can be further dewatered using mechanical operations (Bennoit & Schuster, 1998). It has also been reported that the amount of required flocculants is greatly reduced compared to settling (ibid). This is a consequence of settling requiring flocs larger than 100μm, whilst DAF optimal floc size ranges between 25 to 50μm (Edzwald & Haarhoff, 2012).

4.3 Application for Industrial Wastewater

DAF has also been used for treating industrial effluents. In fact, the paper industry was one of the earliest to adapt DAF for its wastewater treatment as the characteristics of the effluents were particularly suitable for this technology (Edzwald & Haarhoff, 2012). Dairy, meat, poultry, and oil production industries have also used the technology in their processes (ibid). These applications are relatively well-established compared to its use in mining operations.

It is generally accepted that microbubbles cannot replace the coarse bubbles used in froth flotation because of their relatively weak lifting force and the high suspended solids content in mining mills. A combination of DAF and conventional froth flotation, however, resulted in improved recovery of certain metals (Rodrigues & Rubio, 2007). Although this tendency has been observed in several studies, particularly for fine fractions, it has also been observed that microbubbles also float gangue, thus rendering this use implausible (ibid). Another possibility is using microbubbles to recover very fine and coarse particles which cannot be recovered through traditional froth flotation due to the restrains of macro bubbles (Yoon et al., 1992). In this case the mineral particle sizes that are generally produced in the mills are not favored and the selectivity of the process is not specified. Consequently, the most probable implementations of DAF are seen in areas where the low selectivity of microbubbles is not an issue, such as purification of effluents.

From these applications, one of the most documented is removal of heavy metal ions, either as ion flotation or as precipitate flotation. In ion flotation, surfactants are used to render the metal species hydrophobic, which allows subsequent removal with the microbubbles. This approach is able to remove several metals, including lead (89.95%), copper (81.13%), cadmium (71.17%), zinc, chrome, and silver (up to 90% under basic pH) (Fu & Wang, 2011). On the other hand, precipitate flotation relies on the formation of a precipitate before removing the particles with the microbubbles. This precipitate is formed either as a hydroxide or a salt, and can yield removals of up to 96.2% (ibid). For example, molybdate anions have been successfully removed from filtrates using ferric chloride and sodium oleate, precipitating as metal oleates in a first stage and as hydroxides in a second step (Rodrigues & Rubio, 2007).

DAF has also been coupled with acid mine drainage treatments in coal mines, using different flocculants after adjusting the pH of the effluent (Rodrigues & Rubio, 2007). The microbubbles were used to separate the precipitated formed after neutralizing the effluent, which additionally required using flocculants (ibid). Besides operation costs, this process has the disadvantage of requiring high recycling rates for optimal operation.

As mentioned in Chapter 3, there have been attempts to remove excess mill reagents –namely xanthates- using DAF. The process comprises adsorbing the xanthate in zeolites modified with copper and subsequently floating these zeolites with microbubbles (Oliveira & Rubio, 2008). This alternative is complicated for the costs of manufacturing the zeolites and for the management of the whole process.

Finally, DAF has found applications in other sectors of the mills. Thanks to its ability to float oils, a mill in Brazil has used the process to clean wastewater polluted with oils from the vehicles and equipment of the mine (Rodrigues & Rubio, 2007). This has been more efficient than settling because DAF is able to separate the oils efficiently even when they are emulsified (ibid).

.

DAF has several features that make the process ideal for mining mills applications. Not only the technology is able to remove fine suspended solids (Rodrigues & Rubio, 2007) that are difficult to remove using conventional settling techniques, but several dissolved metal ions and organic compounds can be removed. Additionally, DAF is technically close to froth flotation, which suggests that the technology would be easily adapted in the mining industry. Of particular importance for this study, when coupled with proper coagulation and flocculation, it is well-suited for removing excess mill reagents –such as xanthate- in wastewaters, an accomplishment that would improve water reuse in froth flotation.

5
CONCLUSIONS OF LITERATURE REVIEW

Removal of excess xanthate from mining wastewaters is a major challenge for mine operators. Not only the excess reagent poses environmental risks, but it prevents recycle of the contaminated wastewater. As a result, a larger volume of fresh water must be used for the flotation of minerals increasing the costs associated with raw materials and waste treatment.

Cleaning the effluents for reuse is, however, difficult due to the complex characteristics of the same and the massive volumes that need to be treated. In addition, there is no single effluent from the process but rather many flows with very different features within the same extraction process. Thus, most modern processes rely on passive treatment of effluents and use of fresh water for the separation process. As lower grade minerals are being mined, more water is needed for the extraction and the availability (cost) of the same has become increasingly important over time.

A promising solution for these issues is DAF. On one side, the flows that can be treated with this technologies have been increasing thanks to its success in the municipal wastewater treatment sector. On the other hand, previous applications in mining wastewaters have shown that microbubbles could be used to remove pollutants of concern in mining effluents. Particularly, it is considered that DAF will have a major role in the design of future froth flotation processes as it is well-suited to remove light colloids and fines (Rodrigues and Rubio, 2007).

Nevertheless, the feasibility to remove xanthate using DAF is yet to be explored. Previous studies focused on using an intermediate sorption step of the xanthate on zeolites before DAF. The process is complex and the costs remain too high to be used in the mills. Therefore, there is a need to determine if xanthate can be removed with a simpler process, ideally only with DAF and conventional coagulation/flocculation pretreatments. This concept is further explored in the following experimental sections.

6
MATERIALS AND METHODS

The experimental approach in this study can be divided as: 1) wastewater characterization, 2) preliminary DAF studies, 3) jar tests, and 4) replica of best performant conditions using DAF. Specific details are discussed in the following sections, but some remarks about the general experimental procedure are discussed before that.

Two sets of jar tests (27 and 45 experiments) were conducted as general statistical factorial experimental designs. With xanthate reduction as main dependent or performance variable, the independent variables in the first set were pH, flocculant type, and origin of wastewater. In the second set, the studied independent variables were coagulant concentration, flocculant type, and origin of wastewater. The general designs and the evaluated levels are summarized in Figure 5.

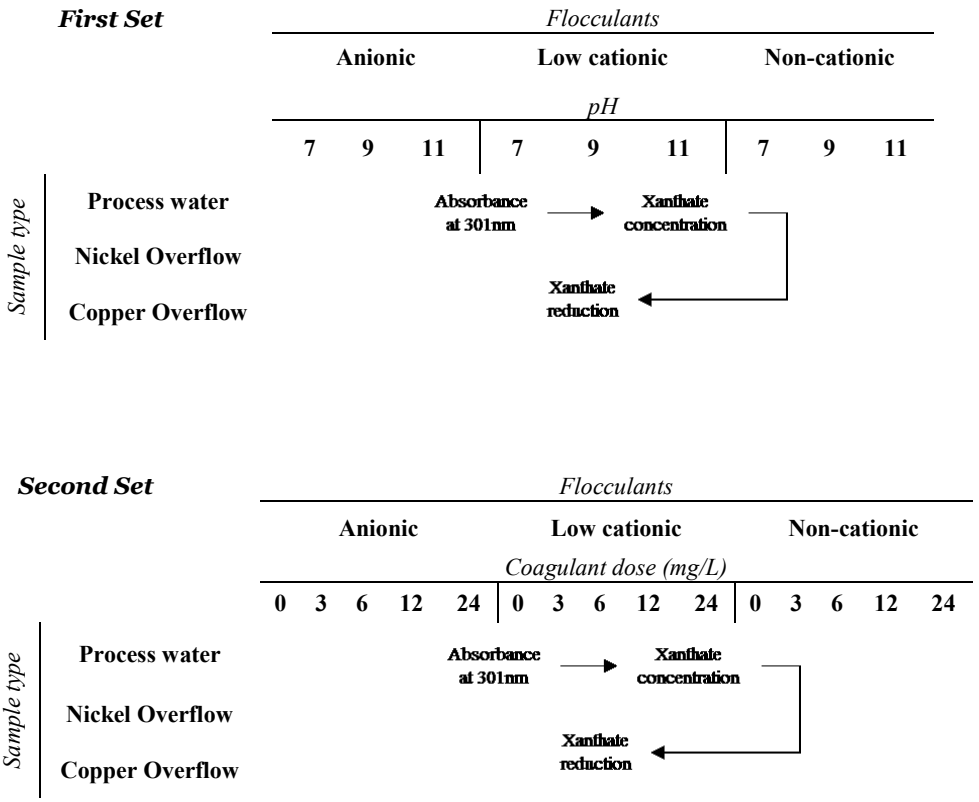


Fig. 5. Experimental design for the jar tests.

Similarly, DAF studies were conducted in two stages. Whilst the first flotation experiments were exploratory, the second stage intended to verify the results observed in the jar tests with DAF.

6.1 Wastewater Samples

The water samples were taken at Kevitsa mine in northern Finland. This mill primarily collects nickel and copper, with an estimated production in 2014 of 9 433 tons and 17 535 tons respectively (FQM, 2014). Said samples were collected from different parts of the mill, as follows:

- overflow wastewater from the nickel concentrate thickener;
- overflow wastewater from the copper concentrate thickener; and
- process water.

Subsequently, the samples were transported to the laboratory in Helsinki for the analyses. All samples were stored at 4°C in the dark before characterization and use.

6.2 Characterization

The wastewater samples were analyzed for UV absorbance at 301 nm, pH, conductivity, redox potential, TOC, suspended solids size distribution, and zeta potential using the equipment described in Table 3.

Table 3. Equipment employed for analyzing wastewater samples

Parameter	Equipment
pH	Orion Star pH Benchtop meter
Conductivity	Orion 150 conductivity meter
Redox potential	Fennolab 3110 meter
TOC	Shimadzu TOC-V CPH analyzer
UV-VIS absorbance	Shimadzu UV-2550 TCC 240A spectrophotometer
Size distribution	Malvern Mastersizer 2000
Zeta potential	Malvern zetaziser ZS90

Additionally, total and dissolved solids were measured gravimetrically. Total solids (TS) were determined by drying 25 mL of sample at 105°C overnight and measuring the weight difference with the initial sample. Dissolved solids (DS) were determined by filtering the samples through glass fiber filters and, subsequently, measuring the weight difference after drying 25mL of the filtered sample at 105°C overnight.

Finally, the elemental composition was determined through inductively coupled plasma optical emission spectrometry, according to standard ISO 11885:2009.

6.3 Preliminary Flotation Studies

6.3.1 Reagents

Potassium ethyl xanthogenate (KEX) was used as xanthate (CS_2O).

Ferric chloride and polyaluminum chloride (PAC) were used as coagulant agents.

In order to evaluate the influence of fines in the process, talc (350 mesh) was used to spike the water.

6.3.2 Procedure

The employed DAF cell is depicted in Figure 6. This apparatus comprises a 10 liters pressure chamber (the saturator) and a 1 liter calibrated cylinder. The pressure in the chamber can be adjusted between 0 and 10 bar, and can be detached from the cylinder.

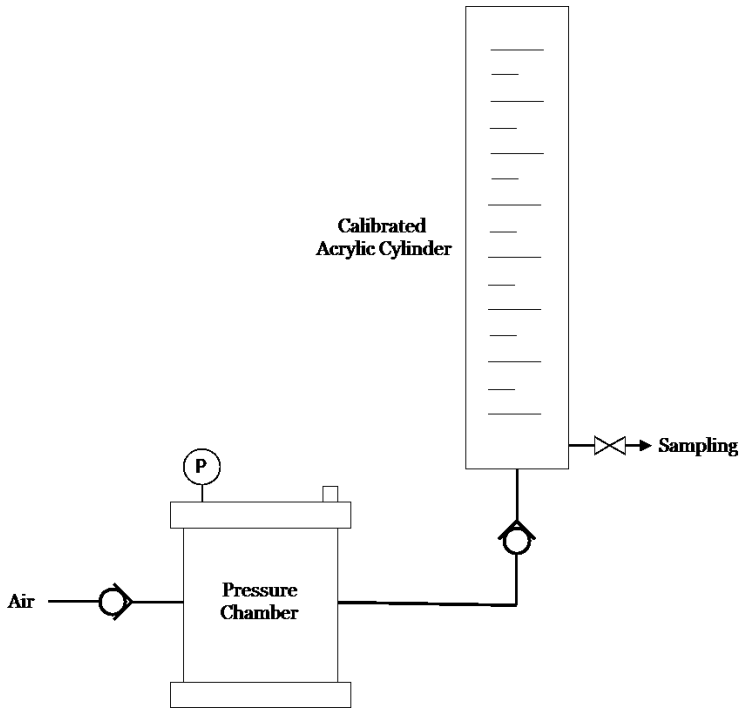


Fig. 6. Diagram of the DAF test equipment.

The flotation tests start by placing a known volume of the sample (usually between 200 and 700 mL) at room temperature in the calibrated cylinder. Distilled water is placed in the pressure chamber and pressurized to 6 bar. Subsequently, this saturated distilled water is released from the pressure chamber into the calibrated cylinder until a volume of 1 L is reached therein. The system is then allowed to stabilize, until the treated sample is transparent and no microbubbles are present in the lower portion of the calibrated cylinder. At this point, samples can be collected for later analysis.

The first preliminary flotation test assessed the effect of microbubbles on xanthate solutions, without any pretreatment. Said solutions comprised about 5 mg/L of CS_2O (from KEX), distilled water, and, optionally, 250 mg/L of talc as fines. As for the conditions of the test, the calibrated cylinder was filled with either 400mL or 600mL of the solutions (with and without talc) for a total of 4 runs. The initial pH was 7 and all runs were conducted at room temperature.

The second preliminary flotation test explored the effect of using only a coagulant before the flotation. The xanthate solutions were as described above, whilst around 30 mg/L of ferric chloride or PAC was added before placing 600 mL of solution (with and without talc) in the flotation cell.

In both cases, samples were collected from the clarified portion and from the overflow. UV-VIS absorption at 301 nm was compared as for assessing the effects after flotation.

6.4 Jar Tests

6.4.1 Reagents

As no xanthate peak was detected in the wastewater samples, KEX was used for replicating the characteristic xanthate levels in the mill.

The employed coagulant was ferric chloride, as 606ppm Fe stock solution. It was prepared one week before the tests and was used within one month.

Three flocculants were used: anionic (Kemira's A100), non-cationic (Kemira's N200), and low-cationic (Kemira's C471). These flocculants were prepared one day before the tests by dissolving 0.5 g of the granulated polymer in 5 mL of isopropanol under fast mixing. Subsequently, 95 mL of Millipore quality water was added to the solution and stirred at medium-low speed until the polymer was completely dissolved. The flocculants solutions were stored at 4°C in the dark and restocked every two weeks.

Calcium hydroxide and sulfuric acid were used for pH adjustment.

6.4.2 Procedure

In the first set of tests, KEX was dissolved in 2.5 L of each sample in order to obtain a CS_2O concentration of about 5 mg/L. Next, 294 mL of this sample was placed in an 800mL glass beaker under a six paddle stirrer. Within two minutes, the coagulant was added to a concentration of 6.06 mg/L of Fe (1:2 molar ratio of CS_2O to Fe) and the pH was adjusted to the desired level (7, 9 or 11, ± 0.25) under intense mixing (200rpm). Subsequently, the rotation of the stirrer was decreased (50rpm) and the flocculant was added to a concentration of 2 mg/L, obtaining in a final volume of approximately 300mL. The sample was stirred slowly for 15 minutes and then allowed to settle, with paddles removed, for 20 minutes.

In the second set of tests, the method was the same as described above with two main differences: the pH was always adjusted to 7 and the concentration of coagulant was adjusted to 0, 3.0, 6.0, 12.1, or 24.2 mg of Fe per L. The volume of the samples was adjusted with Millipore water as for always having a final volume of about 309mL.

The measurements recorded for the samples included pH, turbidity, conductivity, TOC, UV-VIS absorbance at 301 nm, and zeta potential. In the first set of experiments the size of the produced flocs was additionally estimated using a *Malvern mastersizer 2000*. This was done using the lowest flow rate available for the peristatic pump in order to prevent floc breakage.

6.3 Flotation Studies

6.5.1 Reagents

The reagents employed in the jar tests were also used for these studies.

6.5.2 Procedure

The DAF apparatus employed in these studies was that previously described in section 6.3.2.

First, of 5 mg of CS_2O per L were dissolved in 1 L of each sample, using KEX as xanthate source. For each sample 695 mL were transferred to 1 L glass beakers and placed under a six paddle stirrer. Within

two minutes, 25 mg/L of Fe were added and the pH was adjusted to 7 ± 0.25 under intense mixing (150 rpm). Subsequently, the rotation of the stirrer was decreased (50rpm) and the flocculant was added to a concentration of 2 mg/L of flocculant, resulting in a final volume of approximately 700 mL. The sample was stirred slowly for 15 minutes and then allowed to settle, with paddles removed, for 10 minutes. The sample was stirred again at low speed for thirty seconds before transferring 500 mL of the same to the DAF cell. Flotation was conducted with a saturator pressure of 6 bar. An additional sample was tested for comparison, comprising 5 mg of CS_2O and distilled water.

Samples were collected from the bottom of the calibrated cylinder (clarified portion) five minutes after the saturated water was released. UV-VIS absorption at 301 nm was measured in order to estimate the xanthate removal.

7
RESULTS AND DISCUSSION

7.1 Characterization of Wastewater Samples

Table 4 presents the measured parameters of the wastewater samples. Whilst most of these measurements are similar, it is worth noting that the redox potential is significantly lower in the copper overflow sample. It is believed that this difference has important implications on the results of the experiments, as discussed later. Furthermore, particle size distribution for the nickel and copper overflows wastewater is presented in Appendix A.

Table4. Selected parameters of the water samples from Kevitsa Mill

Parameter	Process water	Nickel overflow	Copper overflow
pH	7.2	8.0	10.6
Conductivity (mS)	2.2	2.2	2.3
Redox Pot. (mV)	47.1	64.3	8.8
TS (mg/L)	1471	1598	1716
DS (mg/L)	1471	1494	1532
TOC (mg/L)	25.1	31.0	28.5
TC (mg/L)	31.1	35.3	30.0
IC (mg/L)	6.0	4.3	1.6
COD (mg/L)	102.5	146.9	147.4
Zeta Pot. (mV)	-8.4	-12.5	-3.7

The elemental analysis of the wastewater samples is presented in Table 5. As expected, the nickel and copper levels are relatively high in the overflows samples, with copper concentration exceeding local legal limits in both overflows and surpassing the legal nickel discharge limit for the nickel overflow. It should also be highlighted that the overflows have significantly higher concentrations of iron and phosphorous than the process water.

Table 5. Elemental analysis of the water samples from Kevitsa Mill

Element	Units	Process water	Nickel overflow	Copper overflow
Al	*mg/L*	<0.03	0.18	<0.03
As	*mg/L*	<0.015	<0.015	<0.015
B	*mg/L*	<0.02	<0.02	<0.02
Ba	*mg/L*	0.080	0.072	0.083
Be	*mg/L*	<0.005	<0.005	<0.005
Ca	*mg/L*	139	155	241
Cd	*mg/L*	<0.002	<0.002	<0.002
Co	*mg/L*	<0.003	0.035	0.004
Cr	*mg/L*	<0.01	0.018	<0.01
Cu	*mg/L*	<0.005	0.46	1.23
Fe	*mg/L*	0.041	3.86	2.08
K	*mg/L*	52.1	57.0	56.1

Mg	*mg/L*	59.2	52.0	22.7
Mn	*mg/L*	0.045	0.025	0.028
Mo	*mg/L*	0.012	0.011	0.010
Na	*mg/L*	187	187	186
Ni	*mg/L*	0.056	0.75	0.075
P	*mg/L*	0.18	4.22	3.16
Pb	*mg/L*	<0.015	<0.015	<0.015
S	*mg/L*	195	201	204
Sb	*mg/L*	<0.015	<0.015	<0.015
Se	*mg/L*	<0.015	<0.015	0.016
Sn	*mg/L*	<0.015	<0.015	<0.015
Ti	*mg/L*	<0.015	<0.015	<0.015
V	*mg/L*	<0.005	<0.005	<0.015
Zn	*mg/L*	0.011	0.038	0.031

7.2 Preliminary Flotation Studies

Table 6 shows the effect of DAF without pretreatment on the contaminated samples. It can be seen that for both recycle rates the measured concentration of xanthate is about equal in the clarified and overflow samples, with and without fines (talc). This means that microbubbles alone are not able to remove xanthate from the wastewater. It was observed, however, that the concentration of suspended solids was indeed larger in all overflow samples.

Table 6. Results of preliminary flotation tests for recycle rates (R) of 60 and 40%

		R=60		**R=40**	
		Clarified	**Overflow**	**Clarified**	**Overflow**
[KEX] (mg/L)	Xanthate	2.72	2.68	2.30	2.43
	Xanthate + Talc	3.77	3.72	3.53	3.43

The tests with different coagulants are presented in Table 7. In this case, the xanthate concentration differences between the clarified and overflow samples are greater than in the previous experiment. Particularly, PAC has a noticeable impact when there is no talc (no fines), whilst a greater difference was observed for ferric chloride when there were fines in the samples. As the samples collected from the mill contained fines, it was decided to use ferric chloride in the jar tests.

Table 7. Results of preliminary flotation tests using PAC and FeCl3 as coagulants

		PAC		**$FeCl_3$**	
		Clarified	**Overflow**	**Clarified**	**Overflow**
[KEX] (mg/L)	Xanthate	3.74	3.53	4.10	3.81
	Xanthate + Talc	4.51	4.57	4.54	4.83

7.3 Jar Tests

Figure 7 presents the measured UV-VIS absorbance of aqueous solutions with different xanthate concentrations. This relationship was used to estimate the xanthate concentration in the samples before and after the experiments.

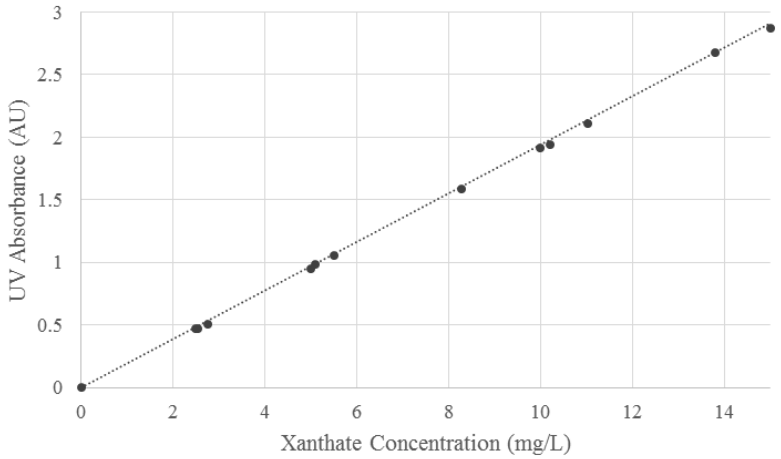


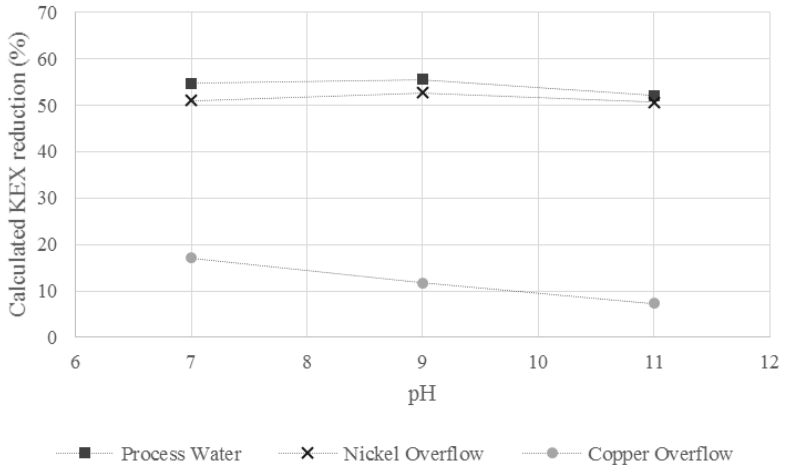
Fig. 7. Relationship between xanthate concentration and UV-VIS absorbance.

During both sets of jar tests, it was observed that the measured initial xanthate concentration did not correspond with the theoretical amount of xanthate that was added to the samples. As shown in Table 8, the measured initial concentration of xanthate was significantly lower for the process water and nickel overflow samples, whereas the copper overflow sample concentration was equivalent. These discrepancies could be caused by the reaction of xanthate with the dissolved compounds of the samples, after which, the new pollutant form cannot be identified through spectrophotometry. The behavior of the copper overflow could be explained by its marked redox potential difference with the other samples. It is well known that said potential has a significant impact on xanthate adsorption on minerals and could have similar effects in this case, preventing reaction of xanthate with the compounds dissolved in the wastewater.

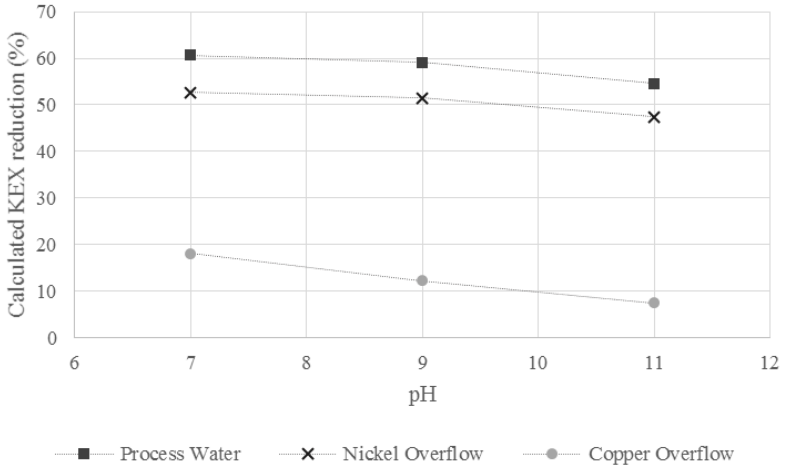
Table 8. Differences between calculated and measured xanthate concentration

Set	Sample	Calculated initial xanthate concentration (mg/L)	Measured initial xanthate concentration (mg/L)
1	Process water	5.33	2.98
	Nickel overflow	5.33	2.75
	Copper overflow	5.33	5.24
2	Process water	5.47	2.27
	Nickel overflow	5.47	3.15
	Copper overflow	5.47	5.64

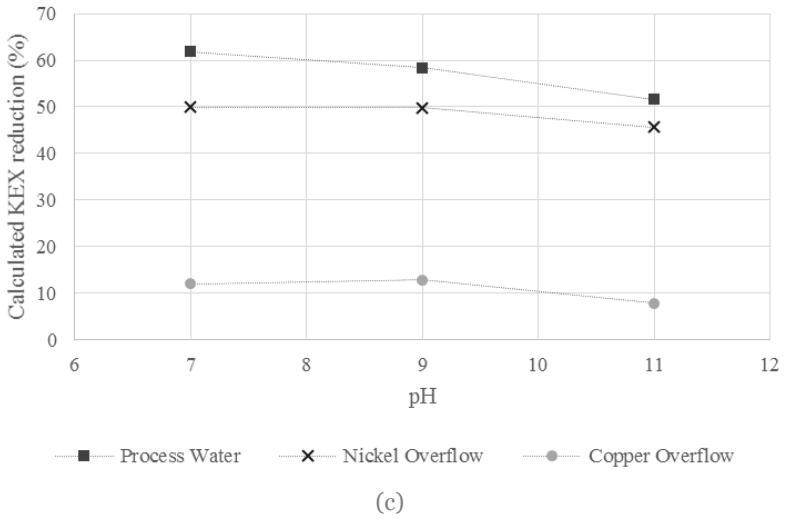
The results of the first set of jar tests are presented in Figure 8 as xanthate reduction at different pH levels for every flocculant. It should be noted that the calculations for said reduction are based on the calculated initial xanthate concentration rather than the measured one. Although this could be overestimating the amount of xanthate removed –since the xanthate that cannot be detected may still be in the clarified wastewater-, the calculations with the measured initial concentration yielded negative reductions in some cases. Therefore, it is believed that the actual reduction is closer to the values shown below.



(a)



(b)



(c)

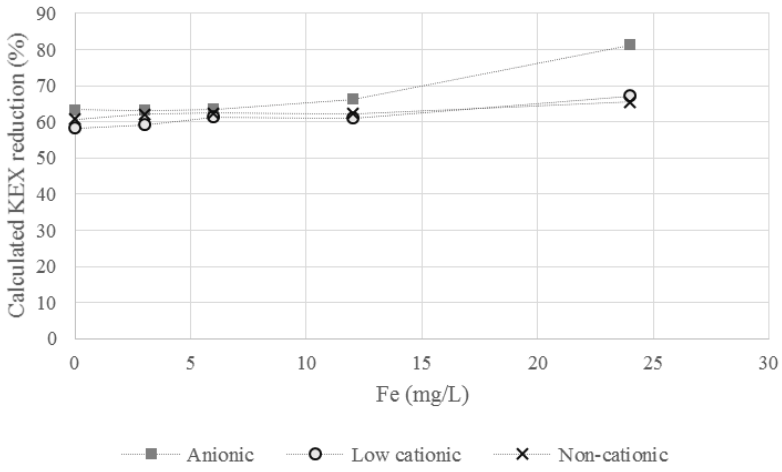
Fig. 8. Effect of pH on calculated xanthate reduction for (a) anionic, (b) non-cationic, and (c) low cationic flocculants.

It is clear from the above that the source of wastewater has a major impact on the xanthate removal, which is confirmed from the ANOVA ($p < 0.0001$). The highest removal was achieved in the process water (~55%), followed by nickel overflow (~50%), and copper overflow (~12%). In these cases, the final xanthate concentrations were 2 mg/L, 2.5 mg/L, and 4.3 mg/L, respectively. Likewise, pH has a significant influence on the reduction ($p < 0.001$), improving the removal with neutral conditions. On the other hand, the flocculant type does not appear to be statistically significant ($p>0.05$) but seems to interact with the type of sample. Although unclear in this set of experiments, this observation was confirmed in the second set of jar tests. The complete statistical analysis for this first set can be found in appendix C.

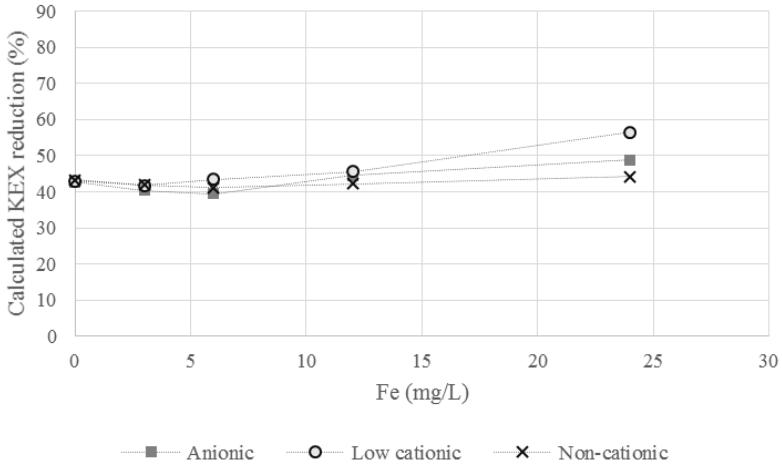
It was also observed that the floc size was not consistent in the experiments. Whilst the majority of flocs agglomerated in the bottom of the jar, a fraction of small flocs were floating naturally after settling. The agglomeration of flocs was greater for pH 7, which also resulted in fewer floating flocs. The Mastersizer measurements shown a floc size of over 150 um which is larger than the recommended for DAF.

Although the zeta potential was reduced in all experiments, the measured amounts were always negative. In other words, a value of zero was not achieved with the 2:1 Fe to CSH2 ratio. The complete zeta potential measurements, as well as turbidity and adsorption can be found in Appendix B.

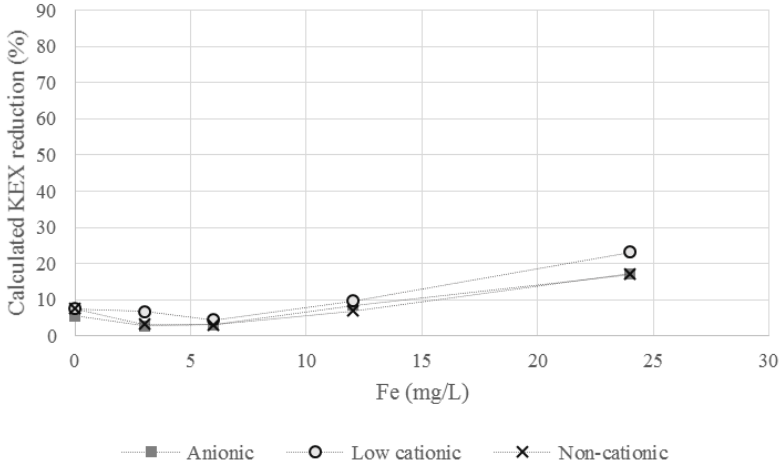
The results of the second set of jar tests are presented in Figure 9 as KEX reduction versus coagulant dose for every flocculant and water sample. Said KEX reduction was calculated in the same manner as for the first set of tests.



(a)



(b)



(c)

Fig. 9. Effect of coagulant dose on xanthate reduction for (a) process water, (b) nickel concentrate overflow, and (c) copper concentrate overflow

These results confirm that the type of wastewater has a major impact on the xanthate removal ($p<0.0001$), with removals of up to 80% for the process water, 56% for the nickel overflow, and 23% for the copper overflow. The measured xanthate concentrations in these cases were 1 mg/L, 2.4 mg/L, and

4.2 mg/L, respectively. Also, the amount of coagulant is statistically significant ($p<0.0001$), having improved removals with increased dose of ferric chloride. As in the previous case, the flocculant is not significant on its own ($p>0.05$), but it interacts with the sample type ($p<0.005$). This indicates that in every sample there is a flocculant that outperforms the others. From Figure 9, it seems that the anionic flocculant is the best for process water, whilst the low cationic yields the best reductions for nickel and copper overflow. The non-cationic flocculant had the lowest reductions for all samples. The complete statistical analysis of these experiments can be found in Appendix E.

Two additional observations are worth commenting regarding this set of experiments. Firstly, it is possible to remove xanthate without adding any coagulant; the flocculant is able to remove the pollutant (about 40%) on its own. Secondly, the zeta potential in this set of experiments reached positive values. Interestingly, xanthate removal continued to increase despite having higher zeta potentials in the final samples. Full measurements can be found in Appendix D.

7.2 Flotation Studies

The results of the replicas of the best performant clarifications using DAF are presented in Table 9. The xanthate reduction with the low cationic flocculant (C471) was lower for the process water, greater for the concentrate copper overflow and about equal for the nickel concentrate overflow.

Table 9. Flotation experiments results

	Distilled water	**Nickel overflow**	**Copper overflow**	**Process water**
C_{init} (mg/L)	5.15	5.15	5.15	5.15
Fe (mg/L)	25	25	25	25
Flocculant	Low cationic	Low cationic	Low cationic	Low cationic
C_{final} (mg/L)	2.67	2.26	2.92	2.58
Reduct. (%)	48.0	56.1	43.2	49.9

It is unclear why the reduction of the copper concentrate overflow sample exhibited such an improvement with DAF. The only parameters that differed from the jar tests were the final volume, the slightly higher concentration of coagulant, and the use of microbubbles. Thus, the addition of more coagulant could have altered the chemistry of the system and allowed greater removals or the mechanisms provided by microbubbles have a large impact on certain wastewater samples. In any case, when taking these results in combination with the distilled water test, it can be affirmed that it is possible to remove around 50% of xanthates from mining wastewater using only DAF with pretreatment.

8
CONCLUSIONS OF EXPERIMENTAL WORK

The results discussed in the previous section demonstrate that it is possible to remove xanthate from mining wastewaters using DAF. The measured reductions were approximately 50% in average, although values of up to 80% were observed. This removal can only be achieved with proper pretreatment of the sample before flotation.

Regarding the conditions of the process, the jar tests indicate that the source of wastewater has the largest impact on the process. Particularly, significantly lower xanthate reductions were observed in the copper overflow wastewater compared to the nickel overflow, process, and distilled water samples. Although this particularity can be attributed to the redox potential differences between the samples, further studies are required before drawing conclusions. Nevertheless, it is clear that the characteristics of the effluent have a major impact on the xanthate removal efficiency.

The tests also showed that the pH of the medium has a significant impact on the xantahte reduction. Whilst neutral values result in higher removals, alkaline pH (9-11) reduces the amount of xanthate that is removed. Thus, in order to maximize xanthate removal it is desirable to clarify the wastewater at a point of the process where the pH of the effluent is neutral.

Likewise, and as expected, increasing the amount of coagulant in the process increases the reduction percentage. However, the measured increment was not particularly large and the employed ferric chloride significantly decreased the pH of the medium. Since relatively high removals were achieved without addition of coagulant, flocculation could be more important for the process than coagulation.

On this regard, the statistical analysis shows that there is a significant interaction between the flocculant and the source of wastewater. The anionic flocculant is the best performing alternative for process water, whilst the low-cationic flocculant is superior for the overflows wastewaters. On the other hand, the non-cationic flocculant exhibited the lowest average removal for all the samples.

Overall, it has been demonstrated that DAF can be used to remove at least one of the pollutants that is hindering water reuse in mining operations. If the xanthate can be removed from the effluents, the wastewater could be used in more sections of the mill, reducing both the amount of fresh water for flotation and the wastewater to the TSF. Therefore, the proposed process has the potential to improve the sustainability of modern mining whilst decreasing the costs, in terms of raw water consumed and sizing of the effluent treatment facilities.

9
RECOMMENDATIONS FOR FUTURE WORK

As previously discussed, certain characteristics of the wastewater allow increased removal of the xanthate. It is essential to determine which these features are in order to design processes able to remove the pollutant efficiently. Specifically, it is suggested to study the impact of redox potential and dissolved metals in the process. As mentioned before, it is well-known that redox potential has a significant impact on flotation by allowing collection of certain minerals. Also, xanthate is able to from complex with metals, some of which could be more easily flocculated in the experiments. Understanding the behavior of the xanthate in different types of wastewater would ultimately result in increased removal efficiencies.

Thus, it is important to comprehend the fate of the xanthate in the wastewater: whether it remains in solution, forms complexes, or dissociates. This can be measured through chromatography (see particularly Ahveninen, 2000) and would provide valuable information for selecting the optimal coagulants and flocculants. Furthermore, this analysis would demonstrate that the xanthate is actually being removed, instead of remaining in the sample as a derivative that cannot be measured with UV-VIS.

As for the jar tests, alternative coagulant/flocculant combinations should be explored as ferric chloride is not yielding significantly larger removals compared with flocculation alone. Even in the case where no improvements are observed, this would still be an indication that no coagulant is required for xanthate removal.

Additionally, the amount of flocculant should be further explored as it is unclear if it has any impact on the xanthate reduction. This could result in an improved process, either by increasing the removal of pollutant or by determining the lowest amount of chemical that yields acceptable removals. Also with the method employed in this study, the resulting flocs are larger than the recommended size for DAF. It is then necessary to adjust the dosing or flocculation method in order to obtain smaller flocs.

From a practical perspective, it is recommended to integrate the flotation cell with the DAF equipment. It was noted that transferring the samples between the devices tends to break the formed flocs and even some agglomerations cannot be transferred due to their size. This does not represent the manner in which the system would work in reality and is, therefore, inducing in errors during the experiments.

Finally, it is suggested further analyzing the samples collected after the treatment for other pollutants that could have been removed. It is known, for example, that turbidity is completely reduced (thus good removal of fines), but it is also believed that several metals are removed. In this case, it is particularly recommended to measure the concentrations of nickel and copper as they were over the local legal discharge limits in the initial samples. If further benefits are observed with the process, scaling of the process is more plausible.

APPENDICES

A. SUSPENDED SOLIDS SIZE DISTRIBUTION

B. MEASUREMENTS FOR FIRST SET OF JAR TESTS

C. ANOVA FOR FIRST SET OF JAR TESTS

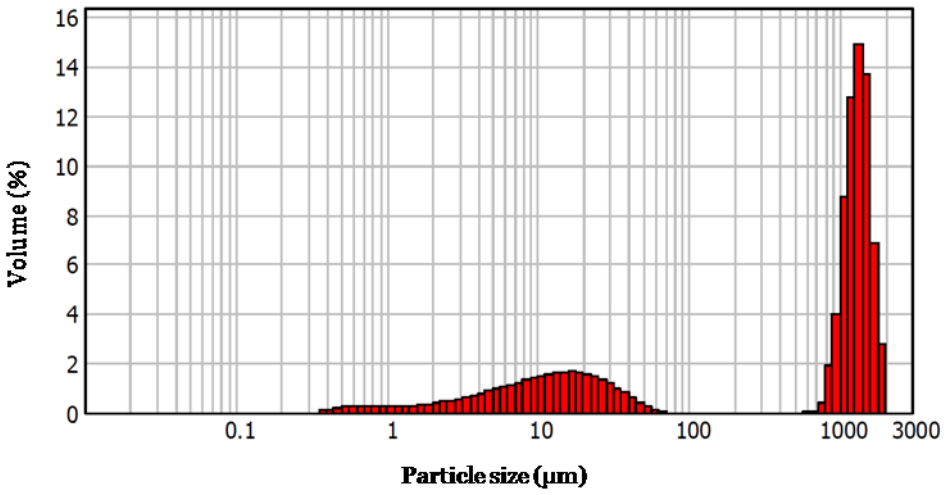
D. MEASUREMENTS FOR SECOND SET OF JAR TESTS

E. ANOVA FOR SECOND SET OF JAR TESTS

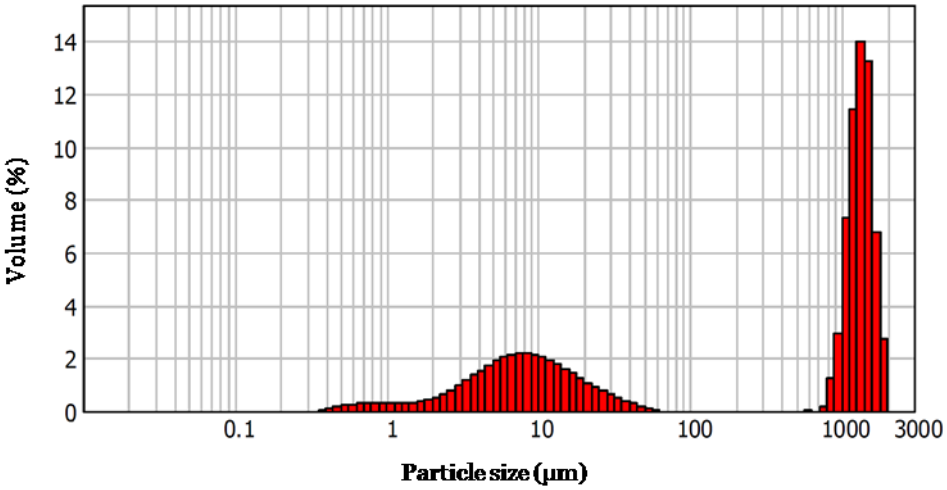
F. FLOCCULATION PHOTOGRAPHS

APPENDIX A

SUSPENDED SOLIDS SIZE DISTRIBUTION



(a)



(b)

Particle size distribution for a) nickel overflow, and b) copper overflow

APPENDIX B

MEASUREMENTS FOR FIRST SET OF JAR TESTS

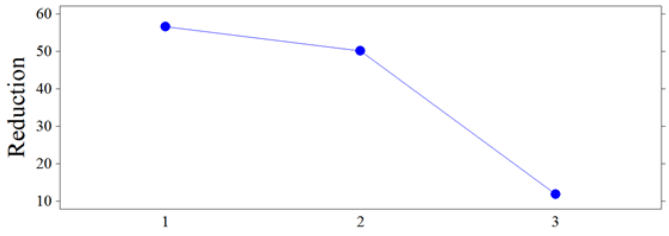
			A100			N200			C471		
		Initial	**pH7**	**pH9**	**pH11**	**pH7**	**pH9**	**pH11**	**pH7**	**pH9**	**pH11**
Process Water	Turb.	0.4	0	0	0	0	0	0.2	0	0	0
	UV	0.817	0.699	0.690	0.725	0.638	0.654	0.699	0.626	0.661	0.730
	Zeta P. (mV)	-8,585	-7,265	-8,49	-10,18	-5,995	-3,905	-3,545	-1.31	-5.7	-10.9
	Floc S. (µm)		135	428	378	307	336	153	302	180	215
Nickel Overflow	Turb.	73.3	0	0	0	0	0	0	0	0	0
	UV	0.705	0.666	0.650	0.671	0.650	0.662	0.703	0.677	0.679	0.721
	Zeta P.	-10,66	-8,69	-8,15	-10,5	-4,58	-5,3	-3,215	-3,96	-5,325	-10,75
	Floc S. (µm)		1049	1190	1328	401	1224	177	262	167	104
Copper Overflow	Turb.	92.8	0	0	0	0	0	0	0	0	0
	UV	1,16447	0.989	1.043	1.088	0.979	1.038	1.086	1.040	1.033	1.083
	Zeta P.	-8.99	-7.54	-7.24	-11.2	-7.095	-4.25	-2.47	-3.26	-3.61	-8.85
	Floc S. (µm)		181	173	218	242	258	240	127	172	213

APPENDIX C

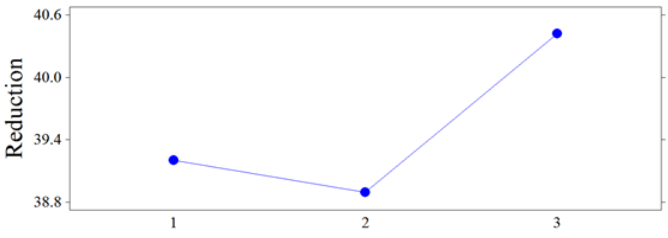
ANOVA FOR FIRST SET OF JAR TESTS

Source	DF	SS	MS	F	P
Flocculant	2	11.7	5.85	1.6	0.2607
Sample	2	101518.4	5259.19	1436.26	0.0000
pH	2	169.9	84.97	23.21	0.0005
Flocculant*Sample	4	33.7	8.42	2.3	0.1470
Flocculant*pH	4	9.4	2.35	0.64	0.6477
Sample*pH	4	19.6	4.90	1.34	0.3357
Error	8	29.3	3.66		
Total	26	10792.0			

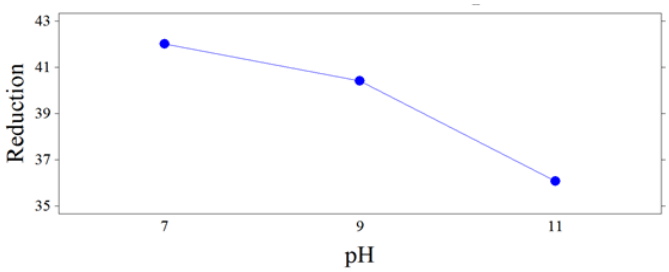
Grand Mean	39.507	CV	4.84	



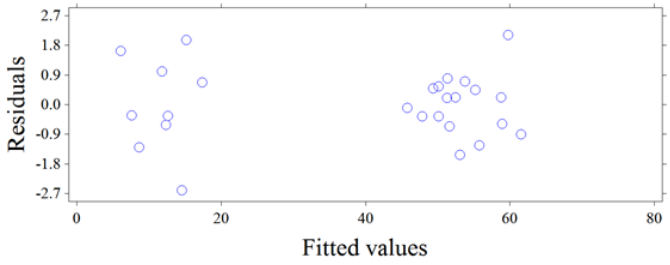
Means of Reduction for Sample



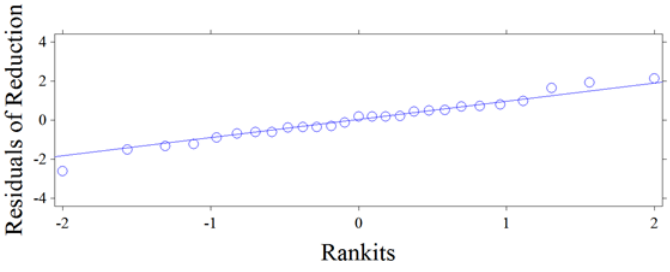
Means of Reduction for Flocculant



Means of Reduction for pH



Residuals by Fitted Values Plot for Reduction



Normal Probability Plot

APPENDIX D

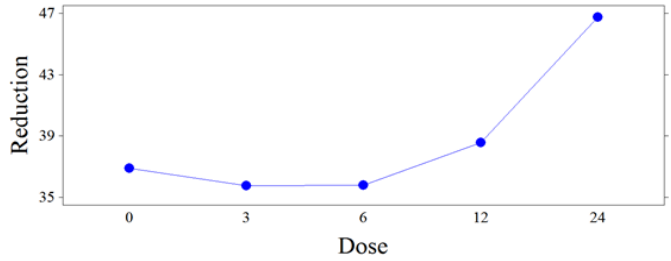
MEASUREMENTS FOR SECOND SET OF JAR TESTS

			Anionic flocculant					Low-cationic flocculant					Non-cationic flocculant				
		Initial	**0**	**3**	**6**	**12**	**24**	**0**	**3**	**6**	**12**	**24**	**0**	**3**	**6**	**12**	**24**
Process water	*Absorbance*	0.441	0.369	0.371	0.368	0.340	0.189	0.421	0.412	0.390	0.394	0.331	0.396	0.383	0.380	0.380	0.348
	Zeta (mV)	-9.56	-8.53	-12.6	-11	-8.97	-10.7	0.286	4.89	1.3	6.72	7.96	-10.3	-9.19	-7.81	-5.94	-3.37
	TOC (mg/L)	25.29	30.7	29.38	29.68	31.82	32.17	28.52	34.48	31.07	31.76	29.58	25.35	23.69	23.76	24.95	22.8
Nickel Overflow	*Absorbance*	0.611	0.597	0.621	0.630	0.577	0.533	0.593	0.606	0.589	0.566	0.453	0.590	0.605	0.612	0.601	0.581
	Zeta (mV)	-6	-6.16	-9.23	-11.3	-10.4	-11.8	-4.31	-1.88	5.23	7.08	6.64	-1.63	-3.49	-3.87	-3.06	-3.17
	TOC (mg/L)	30.39	38.47	39.16	41.84	38.02	39.80	41.2	43.98	43.81	40.68	42.07	41.52	42.78	42.36	40.78	40.5
Copper Overflow	*Absorbance*	1.094	0.982	1.011	1.008	0.953	0.863	0.963	0.969	0.994	0.939	0.799	0.961	1.007	1.007	0.968	0.861
	Zeta (mV)	-1.15	-4.93	-11	-9.18	-10.3	-11.1	-6.3	-4.31	-5.07	-1.73	4.28	-4.19	-3.73	-3.99	-3.5	-3.43
	TOC (mg/L)	29.77	38.47	39.16	41.84	38.02	39.8	37.79	44.46	34.66	38.15	69.29	34.02	34.72	34.72	34.53	33.39

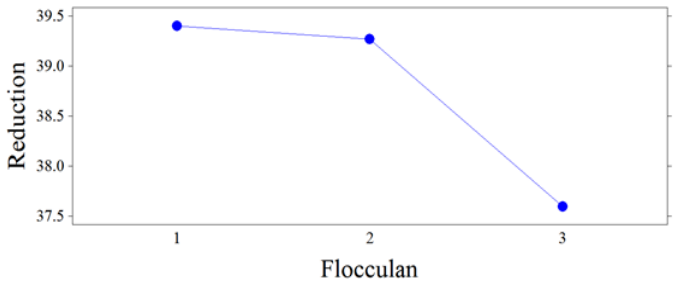
APPENDIX E

ANOVA FOR SECOND SET OF JAR TESTS

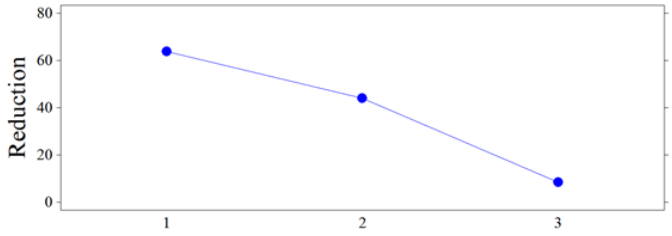
Source	DF	SS	MS	F	P
Dose	4	768.3	192.1	37.29	0.0000
Flocculant	2	30.3	15.1	2.94	0.0819
Sample	2	23633.5	11816.7	2294.27	0.0000
Dose*Flocculant	8	73.5	9.2	1.78	0.1544
Dose*Sample	8	69.8	8.7	1.69	0.1758
Flocculant*Sample	4	136.5	34.1	6.62	0.0024
Error	16	82.4	5.2		
Total	44	24794.2			
	Grand Mean	38.754	CV	5.86	



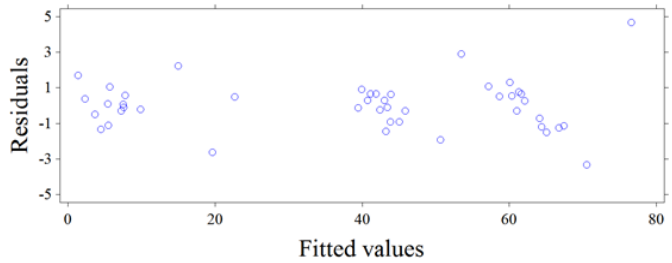
Means of Reduction for Dose



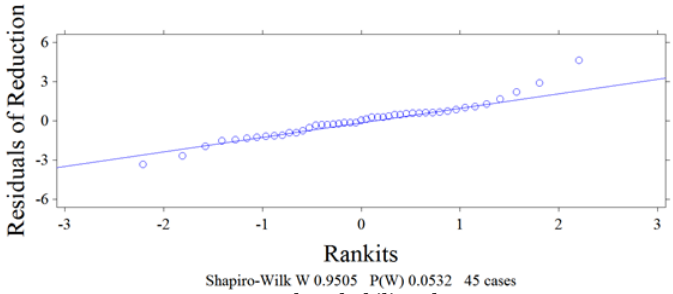
Means of Reduction for Flocculant



Means of Reduction for Sample



Residuals by Fitted Values Plot for Reduction

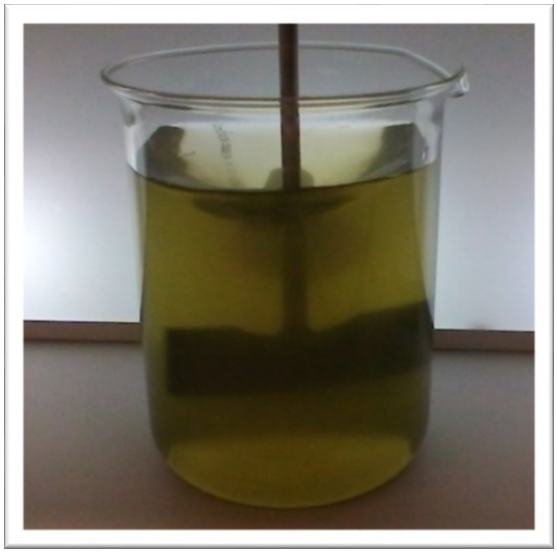


Normal Probability Plot

APPENDIX F

FLOCCULATION PHOTOGRAPHS

(a)



(b)

(c)

(d)

Flocculation process in jar tests for nickel overflow: a) initial sample, b) coagulation with ferric chloride, c) addition of flocculants, d) settling.

REFERENCES

Adiansyah, J. S., Rosano, M., Vink, S., Keir, G. (2015) *A framework for a sustainable approach to mine tailings management: disposal strategies*. Journal of Cleaner Production 108, pp. 1050-1062.

Ahveninen, R. (2000) *The chemical aspects of poor floatability of fine pentlandite*. PhD Thesis. Espoo, Finland: Helsinki University of Technology [published].

Australian Government Publishing Service (1995) *Sodium ethyl xanthate: priority existing chemical No. 5*. Australian Government Publishing Service, Canberra.

Azam, S. (2004) *Thickening of Mine Waste Slurries*. Geotechnical News. December 2004 pp. 40-43.

Bennoit H., and Schuster C. (1998) *Advanced DAF technology for separating and thickening of activated sludge*. STZ Meschede, pp: 1-12.

Bleiwas, D.I. (2012) *Estimated water requirements for the conventional flotation of copper ores: U.S. Geological Survey Open-File Report 2012–1089*, pp. 1-13. Available from: http://pubs.usgs.gov/of/2012/1089/ [referred: 31.12.15].

Boening, D.W. (1998) *Aquatic toxicity and environmental fate of xanthates*. Mining Engineering. 50, 9, pp. 65-68.

Bulatovic, S.M. (2007) *Handbook of flotation reagents: chemistry, theory and practice: flotation of sulphide ores*. Elsevier Science & Technology Books.

Crittenden, J.C., Trussell, R., Hand, D., Howe, K.J., Tchobanoglous, G. (2012) *MWH's water treatment: principle and design* (3rd edition). USA: John Wiley & Sons, Inc.

Dries, J., De Smul, A., Goethals, L., Grootaerd, H., Verstraete, W. (1998) High rate biological treatment of sulfate-rich wastewater in an acetate-fed EGSB reactor. Biodegradation 9, pp. 103-111.

Edzwald, J.K. (2010) *Dissolved air flotation and me*. Water research 44 pp. 2077–2106.

European Commission (2009) *Reference document on best available techniques for management of tailings and waste-rock in mining activities*. European IPPC Bureau.

EPA (2003) *EPA and Hardrock Mining: A Source Book for Industry in the Northwest and Alaska*. United States Environmental Protection Agency. Seattle, United States of America.

First Quantum Minerals Ltd. (FQM) (2014). *2014 Annual Report*. pp.17-29

Fourie, A. B. (2012) *Perceived and realised benefits of paste and thickened tailings for surface deposition*. Paste 2012 – Proceedings of the 15th international seminar on paste and thickened tailings, pp. 53-62.

Fu, F., Wang, Q. (2011) *Removal of heavy metal ions from wastewaters: A review*. Journal of Environmental Management 92; pp. 407-418.

Fuerstenau, M. C., Jameson, G., Yoon, R. (2007) *Froth Flotation: A Century of Innovation*. Society for Mining Metallurgy and Exploration Inc., Littleton, Colorado, USA.

Hao, F., Davey, K.J., Bruckard, W.J., Woodcock, J.T. (2008) *Online analysis for xanthate in laboratory flotation pulps with a UV monitor*. Int. J. Miner. Process. 89 (1-4), pp. 71-75.

IMO (2013) *International Assessment of Marine and Riverine Disposal of Mine Tailings*. International Maritime Organization, London.

International Council on Mining & Metals, (2012). Water management in mining: a selection of case studies. London, UK: ICMM. Available from: https://www.icmm.com/document/3660 [referred 17.11.2015].

Koivunen J., Heinonen-Tanski, H. (2008) *Dissolved air flotation (DAF) for primary and tertiary treatment of municipal wastewaters*. Environmental Technology, 29:1, pp. 101-109.

Lam, K. (1999) *Biodegradation of xanthate by microbes isolated from a tailings lagoon and a potential role for biofilm and plant/microbe associations*. PhD Thesis. Sydney, Australia: University of Western Sydney, Nepean [published].

Larmer, B. (2009). *The real price of gold*. National Geographic. January 2009 [online] Available from: http://ngm.nationalgeographic.com/2009/01/gold/larmer-text/1 [referred: 30.11.2015].

Lupo, J.F., Hall, J. (2010) Dry stack tailings design considerations. AMEC Earth and Environmental. Available from: http://www.infomine.com/publications/docs/Lupo2010.pdf [referred 15.01.2016]

Malley, J.P. (1988) *A fundamental study of dissolved air flotation for treatment of low turbidity waters containing natural organic matter*. University of Massachusetts Amherst.

Metropolitan Council Environmental Services (2007) Recycling Treated Municipal Wastewater for Industrial Water Use. LCMR 05-07d MCES Project No. 070186. Minnesota, United States.

NDM (2005) *Pebble Project Backgrounder: Tailings and Tailings Management*. Northern Dynasty Mines Inc: Pebble Project.

Oliveira, C.R., Rubio, J. (2009) Isopropylxanthate ions uptake by modified natural zeolite and removal by dissolved air flotation. Int. J. Miner. Process. 90, pp. 21–26.

Outotec Oyj (2012) *Outotec® Thickened tailings and Paste Solutions*. Espoo, Finland.

Outotec Oyj (2015) *Holistic solutions for mine tailings and water*. Espoo, Finland.

Ozkan, S.G., Acar, A. (2004) Investigation of impact of water type on borate ore flotation. Water Research Volume 38, Issue 7, pp. 1773–1778.

Palkovits, F. (2008) *Better results from thickened tailings*. Mining Engineering 60, 2, pp. 44-47.

Slatter, K.A., Plint, N.D., Cole, M., Dilsook, V., De Vaux, D., Palm, N., Oostendorp, B. (2009) *Water management in Anglo Platinum process operations: effects of water quality on process operations*. Abstracts of the International Mine Water Conference, pp 46-55.

Seke, M.D., Pistorius, P.C. (2006) Effect of cuprous cyanide, dry and wet milling on the selective flotation of galena and sphalerite. Miner. Eng. 19, pp. 1–11.

Sihvonen, T. (2012) *Determination of collector chemicals from flotation process waters using capillary electrophoresis*. M.Sc. Dissertation. Lapperanta, Finland. Lappeenrannan Teknillinen Yliopisto [published]

Silva A., Varesche, M., Foresti, E., Zaiat, M. (2002) *Sulphate removal from industrial wastewater using a packed-bed anaerobic reactor*. Process Biochemistry 37 (9), pp. 927-935.

Wang, C., Harbottle, D., Liu, Q., Xu, Z. (2014) *Current state of fine mineral tailings treatment: A critical review on theory and practice*. Minerals Engineering 58: 113–131.

Wills, B.A., Napier-Munn, T. (2005) *Wills' Mineral Processing Technology: An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery*, 7th Ed. Elsevier Ltd.

Xingyu, L., Bowei, C., Wenjuan, L., Yongsheng, S., Jiankang, W., Dianzuo, W. (2013) *Recycle of Wastewater from Lead-Zinc Sulfide Ore Flotation Process by Ozone/BAC Technology*. Journal of Environmental Protection, 4, pp. 5-9.

Yoon, R., Adel, G.T., Luttrell, G.H. *Apparatus for the separation of hydrophobic and hydrophilic particles using microbubble column flotation together with a process and apparatus for generation of microbubbles*. United States patent US5397001 A.